

TRANSPORT OF TRACE ELEMENTS IN RUNOFF FROM UNAMENDED AND POND-ASH AMENDED FEEDLOT SURFACES

J. R. Vogel, J. E. Gilley, G. L. Cottrell, B. L. Woodbury, E. D. Berry, R. A. Eigenberg

ABSTRACT. *The use of pond ash (fly ash that has been placed in evaporative ponds for storage and subsequently dewatered) for feedlot surfaces provides a drier environment for livestock and furnishes economic benefits. However, pond ash is known to have high concentrations of trace elements, and the runoff water-quality effects of feedlot surfaces amended with pond ash are not well defined. For this study, two experimental units (plots) were established in eight feedlot pens. Four of the pens contained unamended soil surfaces, and the remaining four pens had pond-ash amended surfaces. Before each test, unconsolidated surface material was removed from four of the plots for each of the amendment treatments, resulting in eight unamended plots and eight pond-ash amended plots. Concentrations for 23 trace elements were measured in cattle feedlot surface material and in the runoff water from three simulated rainfall events. Trace element concentrations in surface material and runoff did not differ between surface consolidation treatments. Amending the feedlot surface material with pond ash resulted in a significant increase in concentration for 14 of the 17 trace elements. Runoff concentrations for 21 trace elements were affected by pond-ash amendment. Sixteen of 21 trace element concentrations that differed significantly were greater in runoff from unamended soil surfaces. Concentrations in runoff were significantly correlated with concentrations in feedlot surface material for boron, manganese, molybdenum, selenium, and uranium.*

Keywords. *Feedlots, Manure runoff, Pond ash, Runoff, Trace elements, Water quality.*

The importance of animal manure management has increased with the intensification of livestock production in concentrated animal feeding operations. Runoff from cattle feedlots may contain microorganisms, nutrients, organic materials, and sediment (Eghball and Power, 1994). Acceptable standards for runoff control from open-lot livestock production facilities have been established through environmental regulations.

A standard feedlot management objective is to maintain a black interface layer of compacted manure above the mineral soil to enhance surface runoff and limit infiltration, thus helping to reduce wet conditions on the feedlot surface (Mielke et al., 1974; Mielke and Mazurak, 1976). To meet this objective, manure may be removed from the feedlot surface between cattle production cycles, usually once or twice a year. Beef cattle feedlots contain unconsolidated surface materials (USM) (loose manure pack) and consolidated sub-surface materials (CSM) (compacted manure, which is anal-

ogous to the black interface layer, and underlying layers) (Woodbury et al., 2001). Unconsolidated surface materials (USM) are thought to be the source of feedlot dust (Miller and Woodbury, 2003). Gilley et al. (2008) found that there were no significant differences in chemical soil characteristics, including Bray-1 phosphorus, calcium, chloride, copper, electrical conductivity, iron, magnesium, manganese, and ammonia, between USM and CSM located within a feedlot near Clay Center, Nebraska.

Coal fly ash is a by-product from coal-fired electrical power generation. Pond ash is fly ash that has been placed in evaporative ponds for storage and subsequently dewatered. Pond ash is much easier to transport than untreated fly ash. The ash is periodically dredged from the ponds and used to make concrete or to build roadbeds.

The constituents of coal ash are primarily oxides of aluminum, calcium, iron, magnesium, potassium, silica, sodium, and titanium. Pond ash also contains trace elements such as arsenic, barium, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, radium, selenium, strontium, uranium, vanadium, and zinc (Zielinski and Finkelman, 1997; Singh and Kolay, 2002; Zhang et al., 2002).

Kalinski et al. (2005) developed construction specifications for the use of fly ash as a feedlot pen construction material. Most of the materials removed from feedlot surfaces between cattle production cycles consist of inorganic soil materials detached and mixed with organic materials by cattle hooves. Much less mixing of surface and subsurface materials occurs on pond-ash amended surfaces. As a result, approximately 14 times more material is required to return the surface to original grade in feedlot pens with an unamended soil surface than in pens with a pond-ash amended surface.

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Woodbury et al. (2007) compared the performance of cattle in feedlots containing unamended soil and pond ash surfaces. Following the feeding cycle, animals were removed and the pens cleaned to approximately the same surface condition. Results indicated that the pens with pond-ash amended surfaces had a 70% reduction in total feedlot manure mass compared to pens with an unamended soil surface.

TRACE ELEMENT TRANSPORT IN RUNOFF

The trace elements in pond ash are exposed to various environmental factors that may affect their solubility, and hence their potential for moving off-site in runoff and becoming available to aquatic organisms. Polic et al. (2005) described four mechanisms that can influence mobility of trace elements:

pH: The increased mobility of the trace elements is usually attributed to an increase in intensity of attachment on the ash mineral phases that contain the elements (Fytianos et al., 1998; Singh and Kolay, 2002; Iwashita et al., 2005; Kim, 2006; Nurchi and Villaescusa, 2008). Singh and Kolay (2002) found that pond ash retained lead from solution; in general, the percent retention of lead increased as the solution pH and contact time with the ash increased. For pH values greater than 4, the measured lead retention was always greater than 90%. Molybdenum, however, is more mobile at higher pH values (Calderone and Frankenberger, 1990; Jankowski et al., 2006). Mobility of selenium in soil is variable depending on both pH and the organic content of the soil (Eich-Greatorex et al., 2007). Many studies have indicated that pH has minimal effect on the mobility of boron (Phung et al., 1979; Ghodrati et al., 1995). In most instances, however, pH is a key factor affecting the mobility of trace elements.

Redox potential: Pond ash in the presence of organic matter can cause microbial oxygen consumption and decrease of redox potential with depth. Consequently, iron and manganese oxides and associated microelements may become dissolved as redox potential decreases. However, as the system becomes more reducing, iron and other trace elements can subsequently be removed via precipitation of sulfide minerals.

Ionic strength: Ionic strength variations will necessarily cause ionic exchange reactions on ash particles. Concentrations of all trace elements extracted generally increase with greater ionic strength of the solvent.

Presence of complexing agents: Some elements can be transformed to more soluble complexes in the presence of agents such as humic substances (Jordan et al., 1997).

Transport of trace elements in urban stormwater runoff has been studied extensively (Makepeace et al., 1995; Mason and Sullivan, 1998; Davis et al., 2001; Vogel et al., 2009). The loss of trace elements from agricultural lands has also been investigated at the watershed scale (Quilbé, 2004; Elra-shidi et al., 2007), field scale (He et al., 2004; Bengtsson et al., 2006), and experimental plot scale (Edwards et al., 1997; Quinton and Catt, 2007). Several studies have shown the utility of using fly ash as an amendment to increase retention of trace elements. Zhang et al. (2008) showed that sand amended with fly ash increased retention of copper, lead, and zinc in bioretention cells used to treat urban stormwater. Lau and Wong (2001) indicated that fly ash decreased the water availability of cadmium, copper, lead, and zinc in fly-ash

amended manure compost. However, Vincini et al. (1994) found greater leaching potential of available manganese and boron in swine manure amended with fly ash compared to unaltered swine manure. Residual chemical constituents contained in the fly ash are thought to have been responsible for the changes in compost and manure characteristics.

Due to present environmental regulations, there is usually no direct hydrologic connection between feedlot runoff and a downstream water body. Some combination of clean water diversion, irrigation systems, runoff collection ponds, and settling basins is typically used for feedlot runoff control. Holding ponds serve to collect and store runoff until it can be land applied. However, for successive storms or for storms larger than the design capacity of the holding pond, runoff water may reach nearby streams. Changes in ionic strength, redox properties, or dissolved organic matter (humic acid) concentrations may affect trace element availability as feedlot runoff moves into lagoons or is applied to land surfaces (Polic et al., 2005).

POTENTIAL ENVIRONMENTAL HEALTH IMPACTS OF POND ASH

El-Mogazi et al. (1988) summarized several studies showing elevated levels of some trace elements in the blood, liver, kidney, muscle, eggs, and other tissues of livestock such as cattle, sheep, pigs, and chickens that were either fed pond ash as part of their diet or fed plants grown on pond-ash amended soil. Van Hassel and Wood (1984) showed that macroinvertebrate populations were negatively affected by trace elements found in a stream receiving coal pond ash effluent. Trace element uptake and phytotoxicity from pond ash have been shown to be a problem for some plants (Aitken and Bell, 1985; Mishra and Shukla, 1986; El-Mogazi et al., 1988; Kukier and Sumner, 1996; Matsi and Keramidis, 1999; Scotti et al., 1999; Chaudhuri et al., 2003). Brieger et al. (1992) found that chromium, selenium, and zinc were bioconcentrated by crickets at a coal fly ash slurry pond site in Michigan. Tadpoles in a coal ash deposition basin also showed oral deformities that limited their ability to graze, and thus their growth rates were impaired (Rowe et al., 1996). Raimondo et al. (1998) showed that bullfrog tadpoles in coal ash ponds exhibited lesser abilities to detect, respond, and escape from predators, perhaps from accumulation of selenium in their muscle tissues.

STUDY OBJECTIVES

At present, little information is available concerning the water-quality characteristics of runoff from pond-ash amended feedlot surfaces. The overall goal of this study was to determine if the use of pond-ash amendment for cattle feedlot pen surfaces affects the transport of trace elements in runoff. The specific objectives of this study were to: (1) measure and compare 23 trace element concentrations in feedlot surface material and in runoff from pond-ash amended and unamended soil surfaces, (2) compare the effects of USM (loose manure pack) and CSM (compacted manure and underlying layers) on trace element transport in runoff, and (3) determine if trace element concentrations in runoff from pond-ash amended and unamended soil surfaces are correlated to trace element concentrations in feedlot surface materials or other trace elements in runoff.

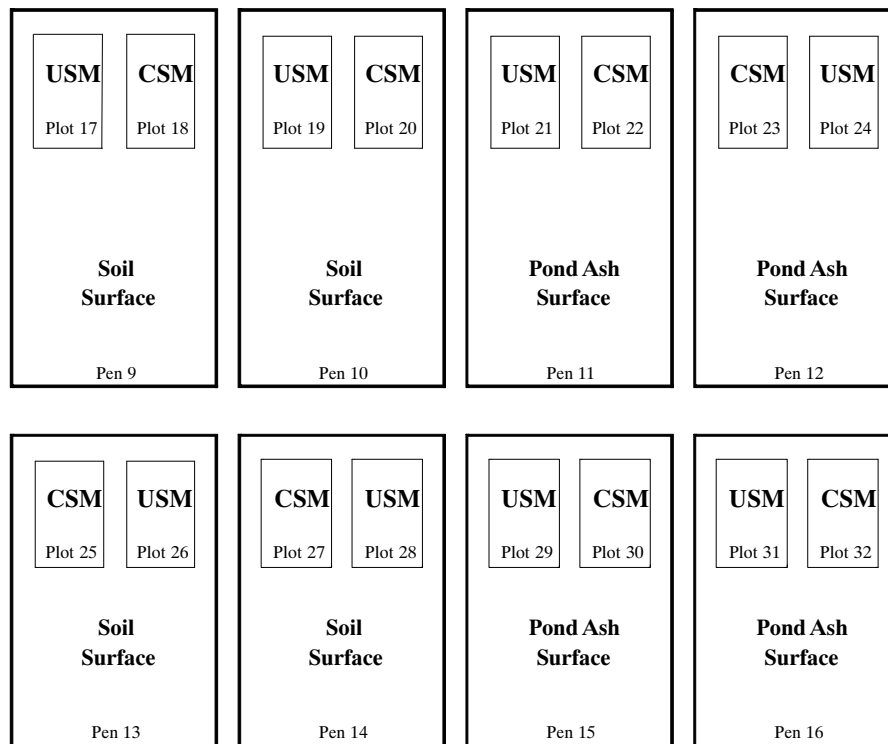


Figure 1. Schematic of the feedlot and plot layout, showing locations of unamended soil surface and pond-ash amended surface feedlot pens (USM = unconsolidated surface material, analogous to loose manure; CSM = consolidated subsurface material, created by removal of USM).

MATERIALS AND METHODS

STUDY SITE

This study was conducted at the U.S. Meat Animal Research Center near Clay Center, Nebraska, during the summer of 2008. Annual mean precipitation at the study site is 728 mm. Experimental units were established within eight 7 m wide × 21 m long feedlots pens (fig. 1). Steer calves born during the spring of 2007 were placed in the feedlot in September 2007 at a rate of eight head per pen (18 m² per head).

Sixteen experimental units (plots) were established in upslope pen locations within areas that allowed overland flow to drain uniformly from the experimental plots. Four of the pens contained an unamended soil surface, and the remaining four pens had a pond-ash amended surface. The feedlot pens were bermed and graded such that runoff from an upslope pen would not run onto a downslope pen (fig. 1). The raw pond ash had been incorporated into these feedlot surfaces three years prior to this study and was no longer available for trace element analyses. Two adjoining 0.75 m wide × 2 m long plots were established within each of the pens. The average slope in the experimental plots was 4.3%, with a standard deviation of 0.8%. Unconsolidated surface material (USM) was removed from one of the two adjoining plots for the CSM treatment. Selection of which of the two adjoining plots had USM removed was random. Thus, a total of eight pond-ash amended and eight unamended soil plots were evaluated. The surface condition of eight of the plots was USM, while the other eight test plots had CSM.

Rainfall simulation tests occurred from May 28 to June 29, 2008. Tests were completed on six plots each week. Livestock from an individual pen were removed just prior to plot establishment, and the pen remained unstocked during the three-day testing period. This was done so that the cattle

would not interfere with the plot or the test equipment while the experimental tests were being conducted within an individual pen. Livestock remained in the adjoining pens until testing within those pens was initiated. By using this procedure, the length of time that expired following removal of cattle among individual pens remained constant. However, the period of time that cattle were on feed varied by a maximum of three weeks.

COLLECTION AND ANALYSES OF FEEDLOT SURFACE MATERIALS

The mass of USM collected from eight of the plots was measured on-site. A subsample of the USM was obtained and stored in a cooler at 4 °C for subsequent analyses. Feedlot surface samples were collected from the outside perimeter of each of the eight test plots with surfaces containing CSM (after the USM had been removed). Composite samples of USM and CSM were sent to the USGS National Water Quality Laboratory in Denver, Colorado, and analyzed for 23 trace elements (table 1).

Feedlot surface samples were prepared for analysis using microwave-assisted acid digestion (USEPA method 3051A, revision 1; Garbarino et al., 2006) and analyzed by inductively coupled plasma-mass spectrometry using USGS method I-4020-05 for all elements except mercury. Surface samples were analyzed using strong acid digestion because on most cattle feedlots, including the one in this study, the conditions in the near-subsurface and in the cattle stomach are capable of reaching pH levels approaching or less than 4 (Diez-Gonzalez et al., 1998). This gives us an idea of the potential for dissolution of the metals in different environments. Mercury was determined by cold vapor-atomic fluorescence spectrometry (USGS method I-4464-01; Garbarino and Damrau, 2001).

Table 1. Laboratory reporting levels for sediment and water, and source water geometric mean concentrations for 23 selected trace elements (LRL = laboratory reporting limit; E = estimated).

Trace Element	Sediment LRL ($\mu\text{g g}^{-1}$)	Water LRL ($\mu\text{g L}^{-1}$)	Source Water Geometric Mean Conc. ($\mu\text{g L}^{-1}$)
Aluminum	0.10	6.0	E3.0
Antimony	0.10	0.40	E0.2
Arsenic	0.10	0.20	1.6
Barium	0.10	0.40	147
Beryllium	0.10	0.02	<0.02
Boron	1.8	14.0	36.2
Cadmium	0.001	0.06	<0.1
Chromium	0.10	0.40	0.74
Cobalt	0.10	0.10	<0.1
Copper	0.10	4.0	29.7
Iron	2.1	14	E10
Lead	0.001	0.10	0.47
Lithium	0.10	0.60	11.8
Manganese	0.30	0.40	0.45
Mercury	0.0072	0.010	E0.005
Molybdenum	0.001	0.10	1.9
Nickel	0.10	0.20	E0.18
Selenium	0.10	0.12	10.5
Silver	0.10	0.06	<0.06
Thallium	0.10	0.12	<0.12
Uranium	0.10	0.02	2.4
Vanadium	0.10	1.6	8.7
Zinc	0.10	2.0	8.8

RAINFALL SIMULATION PROCEDURES

Water used in the rainfall simulation tests was obtained from a hydrant near the feedlot complex and stored in a 3780 L trailer-mounted plastic tank. Water samples were collected from the storage tank once a week during the four-week study period. The pH of source water samples was 8.0. The geometric mean concentration of each trace element measured in the water applied during the rainfall simulation is shown in table 1. Trace element concentrations presented in this article are reported as the difference between the measured runoff concentration and the respective weekly concentration measured in the source water tank.

Rainfall simulation procedures adopted by the National Phosphorus Research Project were employed in this study (Sharpley and Kleinman, 2003). Plot borders consisted of prefabricated sheet metal enclosing three sides of each plot and a sheet metal lip located at the bottom that emptied into a collection trough. All metallic surfaces were painted with non-metallic paint prior to the test, and the trough was lined with plastic that was rinsed with dilute HCl and deionized water prior to each simulation run. The trough extended across the plot and diverted runoff into plastic drums. Two rain gauges were placed along the left edge of the west plot, two rain gauges were placed along the right edge of the east plot, and one rain gauge was located between the paired plots.

A portable rainfall simulator based on the design by Humphry et al. (2002) was used to apply rainfall simultaneously to paired plots. The rainfall simulator operated for 30 min at an intensity of approximately 70 mm h^{-1} . A storm in this area with this intensity and duration has approximately a five-year recurrence interval (Hershfield, 1961). Two additional rainfall simulation runs were then conducted for the same duration and intensity at approximately 24 h intervals. During the

four-week testing period, the research site received a total of 49 mm of rainfall from four separate storms (unpublished data, USDA Meat Animal Research Center, Clay Center, Neb.). However, per the procedures of Sharpley and Kleinman (2003), the runoff plots were wetted prior to each simulation run so that the antecedent moisture content was similar for each of the rainfall simulation runs.

Runoff samples were obtained for trace element analysis using a USGS churn splitter (USGS, variously dated) and preserved on-site using contaminant-free nitric acid. The samples were shipped to the USGS National Water Quality Laboratory and analyzed for the same 23 trace elements that were analyzed in the feedlot surface samples (table 1).

The unfiltered water samples were digested using USGS method I-3486-95 (Hoffman et al., 1996) and analyzed by inductively coupled plasma-mass spectrometry using USGS method I-4020-05 (Garbarino et al., 2006) for all elements except mercury. Mercury was determined by cold vapor-atomic fluorescence spectrometry (USGS method I-4464-01; Garbarino and Damrau, 2001). The water samples were analyzed using strong acid digestion because on most cattle feedlots, including the one in this study, the runoff water will be transported to lagoons that are capable of reaching pH levels approaching or less than 4, especially when operated to reduce ammonia volatilization (Ndegwa et al., 2008).

Six replicates were analyzed for each of the trace elements in water samples. The mean relative standard difference (RSD) between the concentrations in environmental and replicate samples was less than 8%, except for antimony (12%) and silver (29%). Specific conductance and pH were measured in all environmental and source water samples (Johnson and Ulrich, 1959). Raw data from all analyses are archived in the USGS National Water Information System (NWIS) and are available upon request from the USGS Nebraska Water Science Center, Lincoln, Nebraska.

STATISTICAL ANALYSES

Student's t-tests were performed on log-transformed data for all measured properties or concentrations of the feedlot runoff and surface material samples with and without pond-ash amendment. A probability level of <0.05 was considered significant. Correlation matrices were also calculated comparing the trace element correlations between various groupings of surface material and water properties. When using 16 paired observations, a correlation value greater than 0.495 is considered significant (Haan, 2002). All trace element concentration data are archived in the USGS National Water Information System (NWIS).

RESULTS AND DISCUSSION

FEEDLOT SURFACE MATERIAL

The geometric mean concentration for each of the trace elements for the various feedlot surface treatments is shown in table 2. None of the trace element concentrations differed significantly between the USM and CSM feedlot surfaces when comparing all samples, or when comparing only the samples from unamended feedlot surfaces, or when comparing only the samples from pond-ash amended feedlot surfaces ($\alpha < 0.05$) (table 3). Therefore, the consolidation of the surface material did not have an effect on the trace element concentration in the feedlot surface.

Table 2. Geometric mean concentrations of 23 trace elements in feedlot surface samples. All concentrations are in $\mu\text{g g}^{-1}$ (USM = unconsolidated surface material, and CSM = consolidated subsurface material).

Trace Element	Unamended Surface Samples		Pond Ash Amended Surface Samples		All Surface Samples		All Unamended Samples (n = 4)	All Pond Ash Amended Samples (n = 4)
	USM (n = 4)	CSM (n = 4)	USM (n = 4)	CSM (n = 4)	USM (n = 8)	CSM (n = 8)		
Aluminum	16600	16900	24100	21100	20000	18900	16700	22500
Antimony	0.022	0.017	0.010	0.012	0.015	0.014	0.019	0.011
Arsenic	4.65	4.75	6.53	6.26	5.51	5.45	4.70	6.39
Barium	252	247	1396	1347	593	576	249	1371
Beryllium	0.49	0.51	0.83	0.75	0.64	0.62	0.50	0.79
Boron	14.3	15.8	129	105	43.0	40.7	15.1	116
Cadmium	0.28	0.29	0.55	0.44	0.39	0.35	0.28	0.49
Chromium	17.2	17.9	21.7	18.8	19.3	18.4	17.6	20.2
Cobalt	4.93	5.02	7.02	6.42	5.88	5.67	4.97	6.71
Copper	21.8	22.6	53.7	51.1	34.2	34.0	22.2	52.4
Iron	12900	13300	13500	12500	13200	12900	13100	13000
Lead	8.56	8.67	10.7	9.70	9.55	9.17	8.61	10.2
Lithium	11.2	11.6	10.5	10.1	10.8	10.8	11.4	10.3
Manganese	314	314	181	227	238	267	314	203
Mercury	0.012	0.014	0.028	0.024	0.018	0.018	0.013	0.026
Molybdenum	0.83	0.92	1.79	1.88	1.22	1.31	0.87	1.83
Nickel	11.3	11.5	16.2	15.1	13.5	13.2	11.4	15.6
Selenium	0.43	0.46	2.67	2.58	1.08	1.08	0.45	2.62
Silver	0.098	0.089	0.12	0.11	0.11	0.099	0.093	0.11
Thallium	0.25	0.26	0.20	0.17	0.23	0.21	0.26	0.18
Uranium	0.90	0.91	3.06	2.62	1.66	1.54	0.90	2.83
Vanadium	34.9	36.3	63.4	54.2	47.0	44.4	35.6	58.6
Zinc	91.8	95.9	99.1	128	95.4	111	93.8	112

Table 3. Student's t-test probabilities for comparisons of 23 trace element concentrations on various treatments in feedlot surface samples. Probability values less than 0.05 are considered significant. Values in bold are significantly greater for the first treatment in the comparison; values in italics are significantly greater for the second treatment in the comparison (USM = unconsolidated surface material, and CSM = consolidated subsurface material).

Trace Element	All USM surface samples compared to all CSM surface samples	Unamended USM surface samples compared to unamended CSM surface samples	Pond ash amended USM surface samples compared to pond ash amended CSM surface samples	All unamended surface samples compared to all pond ash amended surface samples	Unamended CSM surface samples compared to pond ash amended CSM surface samples	Unamended USM surface samples compared to pond ash amended USM surface samples
Aluminum	>0.5	>0.5	>0.5	<i>0.045</i>	0.16	0.19
Antimony	>0.5	0.23	0.39	0.001	0.21	0.004
Arsenic	>0.5	>0.5	>0.5	<i>0.005</i>	0.035	0.095
Barium	>0.5	>0.5	>0.5	< <i>0.001</i>	< <i>0.001</i>	<0.001
Beryllium	>0.5	>0.5	>0.5	<i>0.004</i>	<i>0.027</i>	0.085
Boron	>0.5	>0.5	>0.5	< <i>0.001</i>	< <i>0.001</i>	0.001
Cadmium	>0.5	>0.5	>0.5	<i>0.007</i>	<i>0.013</i>	0.12
Chromium	>0.5	>0.5	>0.5	0.29	>0.5	0.39
Cobalt	>0.5	>0.5	>0.5	<i>0.037</i>	0.11	0.20
Copper	>0.5	>0.5	>0.5	< <i>0.001</i>	<i>0.010</i>	0.010
Iron	>0.5	>0.5	>0.5	0.92	>0.5	>0.5
Lead	>0.5	>0.5	>0.5	0.21	0.45	0.38
Lithium	>0.5	>0.5	>0.5	0.33	0.34	>0.5
Manganese	0.45	>0.5	0.12	<0.001	0.031	0.005
Mercury	>0.5	0.24	>0.5	<i>0.007</i>	0.13	0.056
Molybdenum	>0.5	>0.5	>0.5	< <i>0.001</i>	<i>0.023</i>	0.018
Nickel	>0.5	>0.5	>0.5	<i>0.017</i>	<i>0.071</i>	0.15
Selenium	>0.5	>0.5	>0.5	< <i>0.001</i>	<i>0.001</i>	<0.001
Silver	>0.5	>0.5	>0.5	0.20	0.37	0.46
Thallium	>0.5	>0.5	>0.5	0.050	<i>0.069</i>	0.41
Uranium	>0.5	>0.5	>0.5	< <i>0.001</i>	< <i>0.001</i>	0.012
Vanadium	>0.5	>0.5	>0.5	<i>0.006</i>	<i>0.026</i>	0.093
Zinc	0.34	>0.5	0.33	0.24	0.28	>0.5

When unamended feedlot surface samples (both CSM and USM) and pond-ash amended feedlot surface samples (both CSM and USM) were compared, 17 trace elements had significantly different concentrations ($\alpha < 0.05$), with 14 of these 17 differences being significantly greater concentrations in the pond-ash amended feedlot surface samples. Concentrations of trace elements in pond-ash amended feedlot CSM samples were significantly greater than the unamended feedlot CSM samples for 12 analyses; only manganese concentration was significantly greater in the unamended feedlot CSM samples. Concentrations of trace elements in pond-ash amended feedlot USM samples were significantly greater than the unamended feedlot USM samples for six analyses; only antimony and manganese concentrations were significantly greater in the unamended feedlot USM samples.

Trace element concentrations of arsenic, beryllium, cadmium, and vanadium were significantly less on the unamended feedlot CSM when compared to the pond-ash amended feedlot by 24%, 32%, 34%, and 33%, respectively. For these four trace elements, concentrations in the USM did not differ based upon having a pond-ash amendment.

FEEDLOT RUNOFF

The geometric mean values in unfiltered runoff for specific conductance, pH, and trace element concentrations for the various feedlot surface treatments are shown in table 4. None of the trace element concentrations in runoff differed significantly between the USM and CSM plots when comparing all

samples or only the samples from pond-ash amended feedlot surfaces ($\alpha < 0.05$) (table 5). Boron was the only trace element with significantly different concentrations in runoff samples between unamended surfaces containing USM and CSM. Runoff concentrations of boron were significantly greater on the unamended surfaces containing USM than on those with CSM. Therefore, except for boron on the unamended plots, the consolidation condition of the surface material does not appear to have a significant effect on the trace element concentration in runoff.

When trace element concentrations between unamended feedlot runoff samples (both CSM and USM) and pond-ash amended feedlot runoff samples (both CSM and USM) were compared, 21 trace elements had significantly different concentrations ($\alpha < 0.05$), with 16 of these 21 trace elements having significantly greater concentrations in the unamended feedlot runoff samples. Vanadium was the only trace element with concentrations that were not significantly different between unamended and pond-ash amended feedlot runoff samples ($p = 0.052$). Mercury was only detected in 13% of runoff samples collected (6 of 48 samples), two samples each in runoff from pond-ash amended USM, unamended CSM, and unamended USM.

Concentrations of trace elements in runoff samples from unamended CSM plots were significantly greater than those in pond-ash amended CSM runoff samples for 11 analyses; five of the trace elements plus specific conductance had significantly greater mean values in the pond-ash amended

Table 4. Geometric mean specific conductance, pH, and trace element concentrations in feedlot runoff samples. All concentrations are in $\mu\text{g L}^{-1}$ unless noted (USM = unconsolidated surface material, CSM = consolidated subsurface material, and NC = not calculated because not enough detections to compute statistics).

Parameter or Trace Element	Unamended Feedlot Runoff Samples		Pond Ash Amended Feedlot Runoff Samples		All Feedlot Runoff Samples		All Unamended Runoff Samples ($n = 24$)	All Pond Ash Amended Runoff Samples ($n = 24$)
	USM ($n = 12$)	CSM ($n = 12$)	USM ($n = 12$)	CSM ($n = 12$)	USM ($n = 24$)	CSM ($n = 24$)		
Specific conductance (mS cm^{-1})	2580	1840	2710	2640	2640	2200	2180	2680
pH (standard units)	7.58	7.78	7.78	7.78	7.68	7.78	7.68	7.78
Aluminum	15200	14500	4220	6720	8000	9870	14800	5320
Antimony	0.29	0.23	0.82	0.65	0.49	0.38	0.26	0.73
Arsenic	35.8	27.1	11.5	14.1	20.3	19.6	31.1	12.7
Barium	631	577	102	224	253	359	603	151
Beryllium	1.14	1.04	0.19	0.30	0.46	0.56	1.09	0.24
Boron	148	104	1650	1320	494	371	124	1480
Cadmium	1.00	1.00	0.26	0.35	0.51	0.59	1.00	0.30
Chromium	18.3	17.5	8.38	11.7	12.4	14.3	17.9	9.92
Cobalt	23.8	20.7	6.35	8.37	12.3	13.2	22.2	7.29
Copper	113	108	45.8	71.9	72.0	88.1	110	57.4
Iron	20800	19900	3170	4570	8130	9520	20300	3810
Lead	27.3	26.0	1.20	2.74	5.74	8.44	26.7	1.82
Lithium	25.1	19.3	0.30	0.96	2.73	4.29	22.0	0.53
Manganese	1226	1098	90.9	138	334	389	1160	112
Mercury	NC	NC	NC	NC	NC	NC	NC	NC
Molybdenum	0.75	0.44	18.4	12.0	3.71	2.31	0.58	14.9
Nickel	62.2	50.9	22.3	28.0	37.3	37.8	56.3	25.0
Selenium	0.14	0.17	1.78	1.76	0.50	0.54	0.15	1.77
Silver	0.10	0.10	0.04	0.07	0.06	0.08	0.10	0.05
Thallium	0.31	0.20	0.05	0.05	0.12	0.10	0.25	0.05
Uranium	0.36	0.32	3.29	3.64	1.09	1.08	0.34	3.46
Vanadium	60.6	54.9	62.1	79.7	61.4	66.1	57.7	70.3
Zinc	421	402	120	170	225	262	411	143

Table 5. Student's t-test probabilities for comparisons of trace element concentrations on various treatments in feedlot runoff samples. Probability values less than 0.05 are considered significant. Values in bold are significantly greater for the first treatment in the comparison; values in italics are significantly greater for the second treatment in the comparison (USM = unconsolidated surface material, CSM = consolidated subsurface material, and NC = not calculated because not enough detections).

Parameter or Trace Element	All USM runoff samples compared to all CSM runoff samples	Unamended USM runoff samples compared to unamended CSM runoff samples	Pond ash amended USM runoff samples compared to pond ash amended CSM runoff samples	All unamended runoff samples compared to all pond ash amended runoff samples	Unamended CSM runoff samples compared to pond ash amended CSM runoff samples	Unamended USM runoff samples compared to pond ash amended USM runoff samples
Specific cond.	0.16	0.090	>0.5	0.11	<i>0.009</i>	>0.5
pH	0.14	0.074	>0.5	0.14	>0.5	<i>0.012</i>
Aluminum	0.44	>0.5	0.23	<0.001	0.061	<0.001
Antimony	>0.5	>0.5	>0.5	<i>0.004</i>	0.051	<i>0.048</i>
Arsenic	>0.5	0.16	0.19	<0.001	<0.001	<0.001
Barium	>0.5	>0.5	0.48	0.019	0.23	0.047
Beryllium	>0.5	>0.5	0.29	<0.001	0.007	<0.001
Boron	0.45	0.001	0.24	<i><0.001</i>	<i><0.001</i>	<i><0.001</i>
Cadmium	>0.5	>0.5	0.32	<0.001	0.007	<0.001
Chromium	0.37	>0.5	0.10	<0.001	0.12	<0.001
Cobalt	>0.5	0.22	0.11	<0.001	<0.001	<0.001
Copper	0.26	>0.5	0.072	<0.001	0.080	<0.001
Iron	>0.5	>0.5	0.24	<0.001	<0.001	<0.001
Lead	>0.5	>0.5	0.35	<0.001	0.002	0.001
Lithium	0.48	0.085	0.071	<0.001	<0.001	<0.001
Manganese	>0.5	>0.5	0.16	<0.001	<0.001	<0.001
Mercury	NC	NC	NC	NC	NC	NC
Molybdenum	>0.5	>0.5	0.34	<i><0.001</i>	<i>0.001</i>	<i>0.004</i>
Nickel	>0.5	0.062	0.15	<0.001	<0.001	<0.001
Selenium	>0.5	>0.5	>0.5	<i><0.001</i>	<i>0.001</i>	<i><0.001</i>
Silver	0.33	>0.5	0.19	0.031	0.42	0.023
Thallium	>0.5	0.32	>0.5	<0.001	0.006	<0.001
Uranium	>0.5	>0.5	>0.5	<i><0.001</i>	<i>0.008</i>	<i>0.015</i>
Vanadium	0.47	0.40	0.13	0.052	<i>0.022</i>	0.85
Zinc	>0.5	>0.5	0.08	<0.001	0.008	<0.001

CSM runoff. The source of the higher specific conductance in pond-ash amended CSM runoff may be higher ionic strength caused by the pond ash. Runoff from USM plots had pH and concentrations of trace elements in unamended feedlot runoff samples that were significantly greater than those in pond-ash amended feedlot runoff for 16 analyses; five of the analyses (including pH) had significantly greater mean values in the pond-ash amended USM feedlot runoff.

Analyses that had significantly different mean values when comparing unamended USM feedlot runoff samples to pond-ash amended USM feedlot surface runoff samples, but not when comparing unamended CSM feedlot runoff samples to pond-ash amended CSM feedlot runoff samples, were pH, aluminum, antimony, barium, chromium, copper, and silver. In runoff, the mean concentrations of these trace elements (except antimony) were less in the pond-ash amended USM feedlot runoff than in the unamended USM feedlot runoff, indicating that pond-ash amendment caused less transport of these trace elements from the feedlot surface in the pens where unconsolidated surface material had not been removed, but not in the pens where unconsolidated surface material had been removed.

When comparing concentrations in runoff from unamended plots to pond-ash amended plots, the only trace element that had significantly different concentrations in runoff samples from CSM plots but not in runoff from USM plots was vanadium. Vanadium concentrations were significantly greater in the pond-ash amended CSM feedlot runoff samples.

SURFACE MATERIAL AND RUNOFF COMPARISONS

Runoff concentrations of aluminum, arsenic, barium, beryllium, cadmium, cobalt, copper, and nickel elements were significantly less on the pond-ash plots than on the unamended feedlot surfaces (table 5). However, concentrations of each of these elements were significantly greater on the pond-ash amended surfaces (table 3). This would indicate that these trace metals were added to the feedlot by the pond-ash amendment but were not transported from the feedlot surface in runoff under the conditions of the rainfall simulation.

Antimony was the only trace element that was significantly less concentrated in unamended soil materials and more concentrated in runoff from the pond-ash amended plots than from the unamended plots. The concentrations of antimony, however, were usually near or below the laboratory reporting limit, and these differences were likely an artifact of the low concentrations. Trace elements that were significantly more concentrated in feedlot surface material and runoff from pond-ash amended plots than from unamended plots were boron, molybdenum, selenium, and uranium. This indicates that these trace elements were added to the feedlot surface by the pond-ash amendment and were transported off the feedlot under the conditions of the rainfall simulation. Manganese and thallium were significantly more concentrated in feedlot surface material and runoff from unamended soil plots than from pond-ash amended plots, indicating that the source of these trace elements was likely the background soil rather than the pond ash.

Table 6 (continued). Correlation values between measured runoff and surface material properties for the complete data set, comprised of eight observations in each consolidated surface material and unconsolidated surface material treatment ($n = 16$). Values are considered significant at a 95% confidence level if they are greater than 0.495; negative values are inversely correlated; highlighted values are significantly correlated (RO = runoff, and SM = surface material).

	SM Al	SM Sb	SM As	SM Ba	SM Be	SM B	SM Cd	SM Cr	SM Co	SM Cu	SM Fe	SM Pb	SM Li	SM Mn	SM Hg	SM Mo	SM Ni	SM Se	SM Ag	SM Ti	SM U	SM V	SM Zn	
SM Al	1																							
SM Sb	-0.373	1																						
SM As	0.957	-0.493	1																					
SM Ba	0.694	-0.655	0.814	1																				
SM Be	0.983	-0.441	0.975	0.794	1																			
SM B	0.861	-0.596	0.891	0.925	0.921	1																		
SM Cd	0.952	-0.387	0.895	0.682	0.956	0.893	1																	
SM Cr	0.978	-0.284	0.896	0.534	0.930	0.756	0.932	1																
SM Co	0.997	-0.376	0.967	0.705	0.986	0.856	0.943	0.971	1															
SM Cu	0.810	-0.570	0.863	0.904	0.884	0.971	0.877	0.710	0.813	1														
SM Fe	0.851	-0.077	0.774	0.312	0.763	0.488	0.700	0.903	0.851	0.424	1													
SM Pb	0.969	-0.293	0.933	0.576	0.935	0.735	0.879	0.972	0.975	0.680	0.929	1												
SM Li	0.675	0.084	0.592	0.048	0.562	0.229	0.516	0.775	0.680	0.192	0.950	0.805	1											
SM Mn	-0.472	0.525	-0.509	-0.783	-0.583	-0.782	-0.580	-0.327	-0.461	-0.718	0.007	-0.310	0.281	1										
SM Hg	0.937	-0.396	0.932	0.753	0.964	0.872	0.925	0.886	0.943	0.832	0.713	0.904	0.531	-0.626	1									
SM Mo	0.283	-0.562	0.438	0.763	0.387	0.652	0.347	0.137	0.285	0.731	-0.083	0.115	-0.272	-0.509	0.284	1								
SM Ni	0.989	-0.419	0.981	0.757	0.991	0.884	0.934	0.948	0.994	0.844	0.826	0.962	0.645	-0.490	0.945	0.356	1							
SM Se	0.636	-0.672	0.763	0.986	0.751	0.915	0.671	0.475	0.647	0.920	0.205	0.501	-0.053	-0.817	0.722	0.806	0.700	1						
SM Ag	0.927	-0.233	0.905	0.620	0.888	0.718	0.781	0.901	0.931	0.639	0.908	0.945	0.758	-0.300	0.828	0.180	0.922	0.516	1					
SM Ti	0.573	0.200	0.413	-0.168	0.432	0.093	0.460	0.714	0.563	0.026	0.863	0.700	0.932	0.306	0.415	-0.505	0.501	-0.257	0.624	1				
SM U	0.921	-0.541	0.940	0.890	0.970	0.984	0.938	0.834	0.922	0.957	0.593	0.826	0.353	-0.732	0.936	0.545	0.939	0.872	0.789	0.220	1			
SM V	0.986	-0.431	0.952	0.757	0.990	0.920	0.979	0.946	0.982	0.879	0.755	0.924	0.553	-0.583	0.955	0.367	0.978	0.721	0.871	0.458	0.965	1		
SM Zn	-0.314	-0.199	-0.168	0.149	-0.223	0.022	-0.180	-0.377	-0.299	0.208	-0.517	-0.424	-0.513	0.033	-0.311	0.698	-0.242	0.250	-0.425	-0.663	-0.078	-0.239	1	

likely transported by similar processes as the salts that caused the specific conductance to change.

Among trace element concentrations in runoff water, aluminum, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, lithium, manganese, nickel, silver, thallium, and zinc were often strongly correlated to one another, indicating that they were probably transported to runoff from similar sources or by similar processes. Similarly, antimony, boron, molybdenum, selenium, and uranium were generally significantly correlated, indicating that they also were probably transported to runoff from similar sources or by similar processes. However, in general, the trace elements in the two groups identified above were negatively correlated with one another. Since both groups came from the same source, this indicates that they were influenced by different transport processes. Trace elements in runoff water that were significantly correlated to only five or fewer other trace elements in runoff water were arsenic (correlated to cobalt, lithium, and nickel and negatively correlated to boron and selenium) and vanadium (correlated to selenium and silver).

Trace element concentrations in feedlot surface material were often correlated to one another. Trace elements in feedlot surface material that were correlated to fewer than ten other trace elements in feedlot surface material were antimony (correlated to manganese and negatively correlated to barium, boron, copper, molybdenum, selenium, and uranium), thorium (correlated to aluminum, chromium, cobalt, lead, lithium, nickel, and silver and negatively correlated to molybdenum and zinc), and zinc (correlated to molybdenum and negatively correlated to iron, lithium, and thorium). This lack of correlation may indicate that these trace elements derived from a different source than the rest of the trace elements (such as from the background soil or manure instead of from the pond ash).

The trace elements that were significantly correlated between runoff and surface material concentrations were boron, manganese, molybdenum, selenium, and uranium. Notably, concentrations of these trace elements (except manganese) were also correlated to each other in feedlot runoff. The availability of boron is generally not pH-dependent (Calderone and Frankenberger, 1990), molybdenum and selenium become more soluble at more alkaline pH values such as what was measured for these samples (Phung et al., 1979; Iwashita et al., 2005), and uranium is generally soluble at the pH range encountered during the present study (Batson et al., 1996).

Boron concentrations in feedlot runoff were also significantly correlated to feedlot surface concentrations of many of the trace element analyzed, with the exception of antimony (negatively correlated), iron, lithium, molybdenum (negatively correlated), silver, thorium, and zinc. This is indicative of these compounds being derived from a similar source (pond ash) in the feedlot surface material, even though many of them were not solubilized into the runoff. Lithium and zinc concentrations in feedlot surface material were not correlated to any trace elements in feedlot runoff, once again indicating that they most likely derived from a source other than the pond ash.

Trace elements in the runoff that were positively correlated to feedlot surface material concentrations for at least ten elements included antimony, selenium, and uranium. Once again, this is another indication that they most likely derived from the same source and were transported by the same processes. Lithium in feedlot runoff was negatively correlated to concentrations of 12 trace elements in feedlot surface material, indicating that lithium likely came from a different source or that its transport was influenced by different variables than these 12 other trace elements.

SUMMARY AND CONCLUSIONS

A study was conducted to determine if amending cattle feedlot surfaces with pond ash affects the transport of 23 trace elements in runoff water. Trace element concentrations in feedlot surface material and runoff were measured for three separate simulated rainfall events on eight USM feedlot plots and eight CSM feedlot plots. Measured concentrations of trace elements in USM and CSM indicated that the consolidation condition of the surface material did not affect trace element concentrations in the surface material or in runoff. However, amending the feedlot surface materials with pond ash had a significant effect on surface material concentrations for 17 trace elements; 14 of the 17 trace elements that had significantly different concentrations were more concentrated in the pond-ash amended plots than in the unamended plots.

A significant effect of pond-ash amendment was found on runoff concentrations for 21 trace elements; 16 of the 21 trace elements that had significantly different concentrations in runoff samples were more concentrated in runoff from unamended plots. When comparing significant differences between unamended plot surfaces and pond-ash amended surfaces, eight trace elements were significantly less concentrated in runoff samples from pond-ash amended plots and significantly more concentrated in the surface samples from pond-ash amended feedlots.

Four trace elements were significantly more concentrated in both runoff and surface samples from pond-ash amended feedlots: boron, molybdenum, selenium, and uranium. The trace elements with significant correlations between their runoff and surface material concentrations were boron, manganese, molybdenum, selenium, and uranium. The pH in runoff water, however, did not show a significant correlation to trace element concentrations in runoff, probably because of the small range of pH (7.5 to 7.8). These experimental results indicate that pond ash can be added as an amendment to feedlot surfaces without substantially impacting the transport of most trace elements in runoff.

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